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Spectroscopic analysis of $LiHoF_4$ and $LiErF_4$

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The polarized absorption spectra for Ho^{3+} and Er^{3+} in $LiHoF_4$ and $LiErF_4$, respectively, have been recorded in the spectral interval 4000–26000 cm^{-1} at 2 K. Parts of the spectra were examined at higher temperatures. The experimental levels for Ho^{3+} and Er^{3+} in $LiRF_4$ were close to those found in $LiYF_4$. The energy levels of the ground-state term for each ion were calculated by diagonalizing in a term basis an effective Hamiltonian, which takes into account the mixing with other terms due to the spin-orbit coupling. The calculations could not give the correct centers of gravity for the multiplets. After the centers of gravity were matched with the experimental centers, the crystal-field parameters were varied to obtain the best agreement with the experimental observations. For Ho^{3+} the agreement obtained was good, but for Er^{3+} it was not possible to get good agreement for the levels of all the multiplets of the ground-state term. With the crystal-field parameters obtained for Er^{3+} when fitting to the levels of the two lowest multiplets only, all the energy levels below 26000 cm^{-1} were calculated by diagonalizing the energy Hamiltonian in a configuration basis. This calculation showed that the term mixing was strong even for the multiplets of the ground-state term. The agreement with the experiments was good for the three lowest terms of Er^{3+}. The fitted values for the crystal-field parameters in $LiRF_4$ were for Ho^{3+} close to the values reported in $LiYF_4$, whereas the parameters differed somewhat in the case of Er^{3+}.

I. INTRODUCTION

The results on Ho^{3+} and Er^{3+} reported here are part of a spectroscopic investigation of rare-earth ions (R^{3+}) in $LiRF_4$, which started with the work on $LiTbF_4$.[1] Results on Er^{3+} diluted in $LIYF_4$ have been reported by Karayianis[2] and on Ho^{3+} diluted in $LIYF_4$ by Karayianis *et al.*,[3] respectively. A few of the lowest levels of Ho^{3+} in $LiHoF_4$ were reported by Battison *et al.*[4]

$LiRF_4$, where R is a rare earth heavier than samarium, crystallizes in the tetragonal scheelite structure. These crystals may be grown with good optical qualities and are of optical interest as well as of magnetic interest. Especially the magnetic properties of $LiHoF_4$ and $LiErF_4$ have been investigated, among others by Hansen *et al.*[5] Further references are collected in Ref. 1.

In Sec. II of this paper the theory for rare-earth ions in crystals is outlined, and the experimental setup is described in Sec. III. Section IV deals with the results on Ho^{3+} and Sec. V with Er^{3+}. Finally, the results are summarized in Sec. VI.

II. THEORY

A. Term Hamiltonian

The energy levels of a single LS term may be approximately found by diagonalizing in the LS basis of the term in question an effective Hamiltonian, which takes into account the perturbation of the spin-orbit interaction by other terms. Note, however, that the true wave functions are not found in this way.

The Hamiltonian is

$$H' = H'_{so} + H'_{cf}\,, \tag{1}$$

where H'_{so} account for the spin-orbit coupling and H'_{cf} for the crystal-field splitting.

Following Karayianis[6] the effective spin-orbit Hamiltonian to order p is given by

$$H'_{so} = \sum_{i=1}^{p} \lambda_i (\vec{L}\cdot\vec{S})^i\,, \tag{2}$$

where λ_i are functions of the spin-orbit parameter ζ and the Slater parameter F_2.

The crystal-field Hamiltonian may be given by

$$H'_{cf} = \sum_i \alpha_i(L) \sum_m B_{im} C_{im}(L)\,, \tag{3}$$

where C_{im} are Racah-operator equivalents and α_i are operator equivalent factors. The crystal-field parameters are denoted by B.

At the rare-earth site in the scheelite structure the symmetry is globally S_4 and locally almost D_{2d}. In both symmetries the only nonvanishing B parameters are B_{20}, B_{40}, B_{44}, B_{60}, and B_{64}, but in S_4 symmetry at least one of the parameters B_{44} and B_{64} must be complex, whereas in D_{2d} symmetry all parameters are real.

B. Configuration Hamiltonian

All the energy levels of the configuration may be found by diagonalizing a Hamiltonian in a basis spanning the whole configuration. Besides giving more levels than the term calculation, this method

should also give the energies with greater accuracy. However, the matrices to diagonalize in the configuration calculation become so great that it is not always possible to use this method.

The Hamiltonian is

$$H = H_{ee} + H_{so} + H_{cf}, \tag{4}$$

where H_{ee} accounts for the electron-electron interaction, H_{so} for the spin-orbit coupling, and H_{cf} for the crystal-field splitting. The Hamiltonian for the electrostatic interaction is given by

$$H_{ee} = \sum_{i>j} \frac{e^2}{r_{ij}}. \tag{5}$$

The matrix elements for this interaction may be expressed as linear combinations of the Slater parameters F_2, F_4, and F_6. However, the ratios between these parameters are rather insensitive to the wave functions, so the three parameters may be reduced to one. With the use of $4f$ hydrogen wave functions $F_4 = \frac{41}{297} F_2$ and $F_6 = \frac{175}{11583} F_2$.

The general spin-orbit Hamiltonian is given by

$$H_{so} = \zeta \sum_i (\vec{l}_i \cdot \vec{s}_i). \tag{6}$$

The crystal-field Hamiltonian may be expressed in the following way:

$$H_{cf} = \sum_{kq} B_{kq} \sum_i (C_i)^{(k)}_q, \tag{7}$$

where $C^{(k)}_q$ are tensor operators normalized like associated Legendre functions.

III. EXPERIMENTAL SETUP

Single crystals of $LiHoF_4$ and $LiErF_4$ were orientated by x-ray technique. Slabs 0.3–0.8 mm thick were cut with faces perpendicular to an a axis and mounted strain-free on a copper plate.

The absorption spectra were recorded using a modified Zeiss MM12 double monochromator. A Glan prism was used as polarizer. The spectral resolution was better than 6 cm^{-1}.

For low-temperature measurements two glass cryostats described elsewhere[7] were used.

IV. $LiHoF_4$

A. f^{10} configuration in the scheelite structure

The ground configuration of Ho^{3+} is $4f^{10}$. According to Dieke[8] the extension of this configuration is 150 000 cm^{-1}, and the center of gravity for the next configuration ($4f^9 5d$) is approximately 70 000 cm^{-1} above the center of $4f^{10}$. Thus for the lowest levels—but only for the lowest—it should be a usable approximation to neglect configuration mixing.

The f^{10} configuration is 1001 times degenerate. According to the three rules of Hund, the ground multiplet is $^5I_8$. However, LS coupling is only an approximation, and for quantitative considerations both LS and J mixing must be taken into account.

In S_4 symmetry the states of a configuration with an even number of electrons transform according to four one-dimensional representations Γ_1, Γ_2, Γ_3, and Γ_4 (in the notation of Koster *et al.*[9]), of which Γ_3 and Γ_4 are related by time-reversal symmetry. Thus the crystal field splits the multiplets in nondegenerate and two times degenerate levels.

Electric-dipole (ED) transitions are parity forbidden within a configuration. However, even a slight configuration mixing makes the ED transitions significant for the rare earth. Magnetic-dipole (MD) transitions are allowed within a configuration, but according to a selection rule on J, ΔJ must be 0 or ±1. Thus MD transitions between most of the multiplets are forbidden when not considering J mixing.

In a crystal there are some additional selection rules for transitions between the different components of the multiplets split by the crystal field. If the radiation is polarized, these rules are rather restrictive. The selection rules for ED transitions in S_4 symmetry are given in Table I.

B. Experimental results

The absorption spectra for polarized light for Ho^{3+} in $LiHoF_4$ were recorded at 2 K in the spectral interval from 4000–26 000 cm^{-1} (2.5–0.38 μm). Special interest was given to the region 4000–14 000 cm^{-1}, which covers the transitions within the ground term, i.e., transitions from $^5I_8$ to $^5I_7$, $^5I_6$, $^5I_5$, and $^5I_4$. These transitions are shown in Fig. 1.

Most of the transitions to the $^5I_7$ multiplet are seen in both polarizations. This is in agreement with the fact that $\Delta J = 1$ for these transitions, and hence MD transitions are allowed. The other transitions within the ground term obey the ED selection rules for S_4 symmetry, which in this special case are the same as for D_{2d} symmetry, since the ground state is degenerate (Γ_3, Γ_4).

As seen from Fig. 1, the crystal field splits

TABLE I. Selection rules in S_4 symmetry for electric-dipole transitions in the case of a configuration with an even number of electrons.

	Γ_1	Γ_2	Γ_3	Γ_4
Γ_1		π	σ	σ
Γ_2	π		σ	σ
Γ_3	σ	σ		π
Γ_4	σ	σ	π	

the multiplets in groups of levels, and some of the lines are so closely spaced that it has been difficult to resolve the splitting. However, it has been possible to give experimental values for most of the levels.

The situation is worse for the transitions to the other terms. The lines of the transitions to $^5F_5$ and $^5F_4$ were disturbed in the high-energy ends by broad bands with heavy absorption, so it has not been possible to determine all the levels of these multiplets experimentally. The intense absorption near the $^5F_5$ lines has also been observed by Karayianis *et al.*[3] in $LiHo_{0.02}Y_{0.98}F_4$. These bands are probably phonon-assisted transitions. They have higher energy than the zero-phonon lines, i.e., phonons are emitted, and this is in agreement with the fact that there are no phonons to be absorbed at 2 K. The occurrence of these transitions may be due to lattice defects.

In the region where the transitions to $^5F_3$ were seen, there were in the low-energy end some additional relative weak but sharp lines. They must be due to impurities. Of the transitions to $^5F_2$ the lines at 21 140 and 21 187 cm^{-1} were very strong.

Most of the lines found in the interval from 21 370–21 500 cm^{-1} occurred in both polarizations, which indicates that J for the corresponding multiplet must be 8 or 7 ($^3K_8$). In the high-energy end of the transitions to $^5G_6$ there was another broad band with strong absorption. According to Dieke[8] this is just the place where $^5F_1$ has to be found.

Below 24 000 cm^{-1} there was some more inexplicable lines. The lines in the interval from 25 900–26 100 cm^{-1} were very sharp, and the corresponding multiplet can with certainty be interpreted as having $J=4$ ($^5G_4/^3G_4$).

To obtain information of the lowest-energy levels of the ground multiplet, parts of the spectra were recorded for temperatures from 10–50 K. Transitions from the six lowest levels were seen, but because of the closely spaced levels it was difficult to get a good determination of the position of these levels. All the experimentally found levels are listed in Table II.

Some of the levels were followed to room temperature, but due to the level at 8 cm^{-1} it was not possible to achieve accurate information of the temperature dependence of the line position. It looked, however, as if the positions were temperature independent within the experimental accuracy.

C. Calculations

The energy levels of the ground term were calculated with the Hamiltonian given in Eq. (1). F_2 was given the free-ion value 415 cm^{-1} (Ref. 10) and ζ and the five real B parameters were varied to obtain the best fit with the experimental levels. As calculations on Tb^{3+} in $LiTbF_4$ have indicated,[1] it is not possible to get a good value for the imaginary part of the B parameters by this procedure. Hence, Im B_{64} was set equal to zero, i.e., D_{2d} symmetry was implicit assumed.

The standard deviation s between the calculated and experimental level position is given by

$$s=\left(\sum_{i=1}^{N}\frac{(\Delta E_i)^2}{N-M}\right)^{1/2}, \tag{8}$$

where N is the number of levels and M is the number of free parameters.

With $p=3$ in Eq. (2) it was, however, not possible to match the centers of gravity for the multiplets and the standard deviation came out higher than 50 cm^{-1}. One way of getting a better s is to

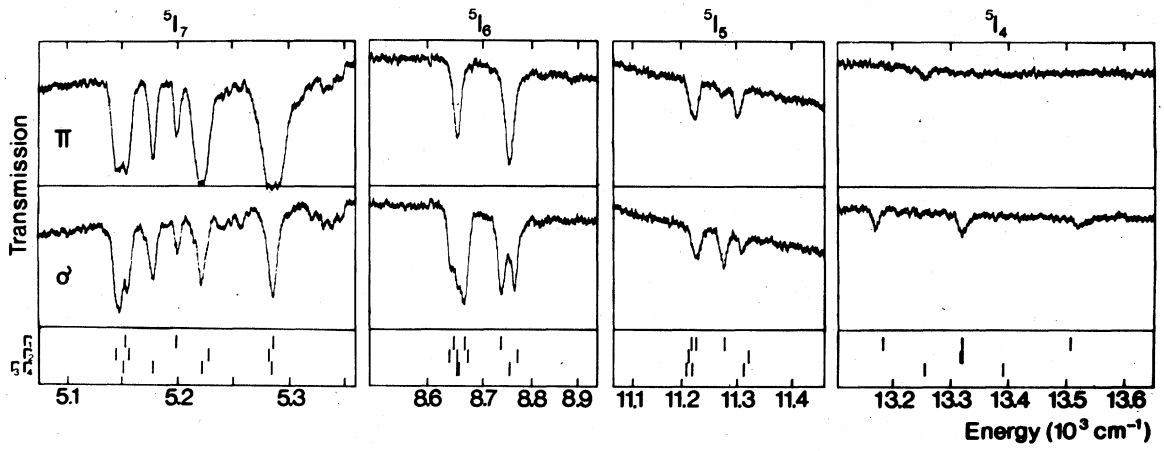

FIG. 1. Polarized absorption spectra at 2 K for Ho^{3+} in $LiHoF_4$ showing the transitions from the ground state to the other multiplets of the ground LS term. In the bottom are given the calculated energy levels found by diagonalizing the matrix of the ground term. The centers of gravity for the multiplets are matched separately.

TABLE II. Experimental energy levels for Ho^{3+} in $LiHoF_4$ below 26 000 cm^{-1}. The absolute uncertainty on the experimental levels is 5 cm^{-1}, whereas the relative uncertainty within a multiplet is 1 cm^{-1} except for the ground multiplet, where it is 5 cm^{-1}. Calculated energy levels of the ground term. The centers of gravity for the multiplets are matched separately.

Polarization	Expt.	$^{2S+1}L_J$	Γ	Calc.
•••	0	$^5I_8$	34	0
•••	8		2	8
•••	26		2	20
•••	49		1	50
•••	61		1	59
•••	78		34	72
			1	211
			1	273
			34	275
			2	284
			34	294
			1	296
			2	310
πσ	5 146	$^5I_7$	2	5 145
πσ	5 148		34	5 151
πσ	5 154		2	5 156
			1	5 161
π	5 177		34	5 178
πσ	5 200		1	5 198
πσ	5 221		34	5 221
π	5 225		2	5 227
π	5 281		2	5 281
πσ	5 285		34	5 284
π	5 291		1	5 285
σ	8 644	$^5I_6$	2	8 640
σ	8 650		1	8 648
π	8 656		34	8 655
			34	8 656
σ	8 657		2	8 655
σ	8 668		1	8 668
			2	8 674
σ	8 735		1	8 733
π	8 749		34	8 749
σ	8 759		2	8 763
πσ	11 219	$^5I_5$	34	11 211
			2	11 215
			1	11 219
π	11 227		34	11 221
σ	11 228		1	11 227
σ	11 278		1	11 279
π	11 304		34	11 313
π	11 310		2	11 323
σ	13 185	$^5I_4$	1	13 184
π	13 260		34	13 258
σ	13 321		2	13 320
			2	13 324
			1	13 329
			34	13 391
σ	13 520		1	13 510

TABLE II. *(Continued)*

Polarization	Expt.	$^{2S+1}L_J$	Γ	Calc.
σ	15 485	$^5F_5$		
π	15 495			
σ	15 505			
σ	15 550			
π	15 605–15 700			
σ	15 630–16 640			
σ	18 490	$^5S_2$		
π	18 507			
σ	18 511			
σ	18 613	$^5F_4$		
π	18 621			
π	18 689			
σ	18 689–18 720			
π	18 717			
σ	20 632	$^5F_3$		
πσ	20 638			
π	20 650			
πσ	20 667			
σ	20 710			
σ	20 757			
πσ	20 768			
σ	21 140	$^5F_2$		
π	21 187			
σ	21 216			
π	21 371	$^3K_8$		
πσ	21 380			
σ	21 390			
πσ	21 400			
σ	21 418			
πσ	21 453			
πσ	21 473			
πσ	21 483			
πσ	21 497			
σ	22 137	$^5G_6$		
π	22 143			
σ	22 156			
σ	22 247			
σ	22 297			
πσ	22 316			
σ	22 362			
π	22 381			
σ	22 393–22 466			
π	22 466	$^5F_1$		
π	23 982	$^5G_5$		
σ	23 989	$(^3G_5)$		
πσ	23 997			
π	24 005			
σ	24 029			
π	24 081			
σ	24 087			
π	24 092			
σ	24 124			
π	24 158			
σ	24 186			

TABLE II. *(Continued)*

Polarization	Expt.	$^{2S+1}L_J$	Γ	Calc.
σ	25 908	$^5G_4$		
π	25 959			
πσ	25 978			
σ	26 018			
σ	26 067			

let λ_1, λ_2, and λ_3 vary independently, but this has no physical meaning. Instead it was decided to vary the B parameters only and to fix ζ on the best value obtained in the first fit. This value was 2140 cm^{-1} (Wybourne[10] gives the free-ion value to 2163 cm^{-1}). The centers of gravity were then matched separately. In this way a standard deviation of 5 cm^{-1} was obtained when fitting to 41 levels. With the experimental uncertainty in mind, a much better agreement could not be expected.

The crystal-field parameters obtained are given in Table III, and the corresponding energy levels are listed in Table II. The calculated level positions are also inserted in the bottom of Fig. 1. The offsets of the centers of gravity for the multiplets are: ($^5I_8$: 0 cm^{-1}), $^5I_7 = -82$ cm^{-1}, $^5I_6 = -119$ cm^{-1}, $^5I_5$: -86 cm^{-1}, $^5I_4$: 64 cm^{-1} (negative values means that the calculated energies were too high).

D. Discussion

Karayianis *et al.*[3] give the experimental energy levels below 21 250 cm^{-1} for Ho^{3+} in $LiYF_4$. The splittings of the multiplets in the diluted crystal are within a few cm^{-1} equivalent to the splittings found in the dense crystal. Somewhat higher differences in centers of gravity for some of the multiplets must be due to experimental inaccuracies.

Karayianis *et al.*[3] have calculated the energy levels below 26 250 cm^{-1} in multiterm model. Their results are in good agreement with the experimental data—even with the levels above 21 250 cm^{-1} reported here for the dense crystal. The crystal-field parameters obtained do not differ more than 30 cm^{-1} from those given here, except for B_{64}, which they allow to be complex. This shows that the crystal-field potential at the Ho site cannot differ much from $LiYF_4$ to $LiHoF_4$.

TABLE III. Crystal-field parameters in cm^{-1} for Ho^{3+} in $LiHoF_4$. The uncertainty on the parameters is less than 10 cm^{-1}.

B_{20}	B_{40}	B_{44}	B_{60}	B_{64}
379	−626	831	−52	608

It should be noted that the parameters in the diluted crystal are fitted to the levels of all the multiplets below 21 250 cm^{-1}.

The assignments in Table II of quantum numbers to the upper multiplets are done with help of the calculations of Karayianis *et al.*[3]

V. $LiErF_4$

A. f^{11} configuration in the scheelite structure

The ground configuration of Er^{3+} is $4f^{11}$. The extension of this configuration is 90 000 cm^{-1} and the center of gravity for the next configuration ($4f^{10}5d$) is approximately 80 000 cm^{-1} above the center of $4f^{11}$.[8] The f^{11} configuration is 364 times degenerate. The ground multiplet is $^4I_{15/2}$.

In S_4 symmetry the states of a configuration with an odd number of electrons transform according to four one-dimensional representations of the double group, Γ_5, Γ_6, Γ_7, and Γ_8.[9] They are related two and two by time-reversal symmetry, so the crystal field splits the multiplets in two times degenerate levels.

The selection rules for ED transitions between these levels are given in Table IV.

B. Experimental results

The absorption spectra for polarized light for Er^{3+} in $LiErF_4$ were recorded at 2 K in the spectral interval from 4000 to 26 000 cm^{-1}. Special interest was given to the region 4000–13 000 cm^{-1}, which covers the transitions from $^4I_{15/2}$ to the other multiplets of the ground term: $^4I_{13/2}$, $^4I_{11/2}$, and $^4I_{9/2}$. These transitions are shown in Fig. 2.

In the whole interval the only lines found were those which were expected for Er^{3+}. The transitions—except those to $^4I_{13/2}$ where $\Delta J = 1$ and MD transitions are allowed—obeyed the ED selection rules.

The linewidths of most of the transitions to levels above the ground term were 10–15 cm^{-1}. Exceptions were the transitions to $^4F_{3/2}$, which were very strong. (These transitions have $\Delta J = 6$, just the same as the strong transitions to $^5F_2$ of Ho^{3+}.)

Thus, contrary to the case of Ho^{3+}, it was

TABLE IV. Selection rules in S_4 symmetry for electric-dipole transitions in the case of a configuration with an odd number of electrons.

	Γ_5	Γ_6	Γ_7	Γ_8
Γ_5		σ	π	σ
Γ_6	σ		σ	π
Γ_7	π	σ		σ
Γ_8	σ	π	σ	

possible to resolve the splittings of the multiplets and experimentally assign J values to them. Further, it was possible to get good information from the warm-up spectra.

Part of the spectra were recorded for temperatures from 10–50 K, and the positions of the four lowest levels for Er^{3+} were determined with good precision. All the levels obtained experimentally are listed in Table V.

The temperature dependence of some of the Er^{3+} lines was examined closely up to room temperature. It was found that the variation of position with temperature was less than 0.02 cm^{-1}/K. The broadening of the lines with increasing temperature was also small.

C. Calculations

The energy levels of the ground-state term were calculated with the Hamiltonian given in Eq. (1). F_2 was given the free-ion value 433 cm^{-1},[10] whereas ζ and the five real B parameters ($\mathrm{Im}\,B_{64} \equiv 0$) were varied to obtain the best fit with the experimental levels.

As in the case of Ho^{3+}, it was not possible to match the centers of gravity for the multiplets by use of an effective spin-orbit Hamiltonian to third order ($s > 100$ cm^{-1}). The best value of ζ was 2325 cm^{-1} (Wybourne[10] gives the free-ion value to 2395 cm^{-1}). When the centers of gravity were matched separately, it was still not possible to get a standard deviation better than 19 cm^{-1} (and only 21 levels were to fit compared to 41 for Ho^{3+}). The B parameters found are given in Table VI, and the calculated level positions are inserted in the bottom of Fig. 2. The offset of the centers of the multiplets are: $^4I_{13/2}$: 116 cm^{-1}, $^4I_{11/2}$: 42 cm^{-1}, and $^4I_{9/2}$: −118 cm^{-1}.

To get a better fit it was tried to let $\mathrm{Im}\,B_{64}$ vary freely too, but this caused B_{20} to take an abnormally low value, and s was only lowered ~2 cm^{-1}.

To investigate the reason for this bad agreement, the Hamiltonian given in Eq. (4) was diagonalized in a basis spanning the ground configuration. The calculation revealed that the upper multiplets of the ground term were heavily mixed with other multiplets (e.g., "$^4I_{9/2}$" contained less than 50% ^4I). This explains why it was not possible to obtain a good fit for the B parameters to the whole ground term.

A new fit with the Hamiltonian of Eq. (1), where only the two lowest multiplets were taken into account, gave a standard deviation of 5 cm^{-1} (a good agreement was of course to be expected, since there were six parameters to fit 11 levels). The new B parameters are given in the second row of Table VI. It is seen that these parameters deviate considerably from the first set of parameters obtained, but they are close to the parameters for Ho^{3+}, as should be expected for two neighboring ions.

With the last set of parameters some further configuration calculations were performed. Calculations with different F_2 values showed that the splitting of the ground term was sensitive to this

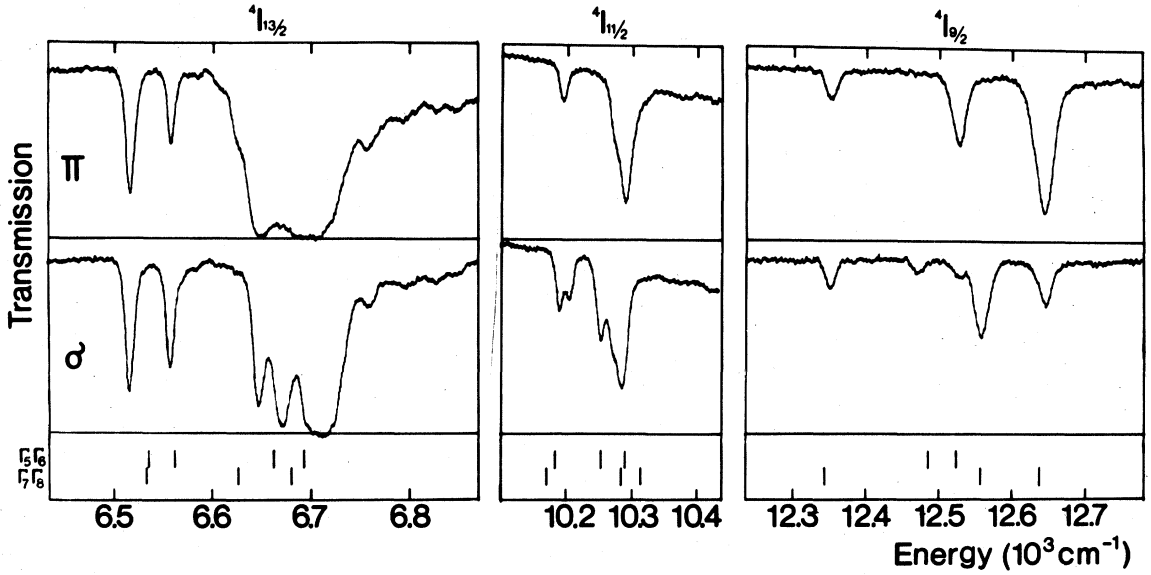

FIG. 2. Polarized absorption spectra at 2 K for Er^{3+} in $LiErF_4$ showing the transitions from the ground state to the other multiplets of the ground LS term. In the bottom are given the calculated energy levels found by diagonalizing the matrix of the ground term with use of the first set of crystal-field parameters listed in Table VI. The centers of gravity for the multiplets are matched separately.

TABLE V. Experimental and calculated energy levels in cm^{-1} for Er^{3+} in $LiErF_4$ below 26 000 cm^{-1}. The absolute uncertainty on the experimental levels is 5 cm^{-1}, whereas the relative uncertainty within a multiplet is 1 cm^{-1}. The second set of crystal-field parameters listed in Table VI is used in the calculations. The W, U numbers of the terms with equal L and S are as follows: $^2H1$: (210)(11), $^2H2$: (210)(21), $^2G1$: (210)(20), $^2G2$: (210)(21), $^2D1$: (210)(20), $^2D2$: (210)(21). S is the standard deviation between experimental and calculated splittings of the multiplet with the centers of gravity matched. Δcg is the mismatch between the centers of gravity.

Polarization	Expt.	J	Γ	Calc.	Wave functions	S	Δcg
•••	0	$\frac{15}{2}$	56	0	96% ^4I, 4% ^2K	4	0
•••	18		78	16			
•••	20		56	21			
•••	60		78	50			
			78	232			
			78	273			
			56	305			
			56	334			
$\pi\sigma$	6 516	$\frac{13}{2}$	78	6 785	99% ^4I, 1% ^2K	5	−266
			56	6 789			
$\pi\sigma$	6 558		56	6 819			
$\pi\sigma$	6 640		78	6 907			
σ	6 670		56	6 938			
π	6 687		78	6 956			
$\pi\sigma$	6 711		56	6 975			
$\pi\sigma$	10 193	$\frac{11}{2}$	78	10 243	77% ^4I, 2% $^2H1$,	7	−44
σ	10 203		56	10 256	19% $^2H2$, 1% ^2I,		
σ	10 253		56	10 296	1% ^4G		
$\pi\sigma$	10 266		78	10 312			
			56	10 322			
$\pi\sigma$	10 290		78	10 329			
$\pi\sigma$	12 350	$\frac{9}{2}$	78	11 927	42% ^4I, 5% $^2H1$,	5	424
σ	12 470		56	12 054	20% $^2H2$, 11% $^2G1$,		
$\pi\sigma$	12 526		78	12 102	7% $^2G2$, 15% ^4F		
σ	12 554		56	12 123			
$\pi\sigma$	12 642		78	12 218			
$\pi\sigma$	15 280	$\frac{9}{2}$	78	15 334	51% ^4F, 34% ^4I,	6	−47
σ	15 300		56	15 354	8% $^2G1$, 4% $^2G2$,		
$\pi\sigma$	15 320		78	15 365	2% $^2H2$		
$\pi\sigma$	15 386		78	15 429			
σ	15 440		56	15 479			
σ	18 423	$\frac{3}{2}$	56	18 319	59% ^4S, 20% ^2P,	2	102
$\pi\sigma$	18 480		78	18 380	11% $^2D1$, 7% ^4F,		
					2% $^2H2$, 1% ^4G		
σ	19 146	$\frac{11}{2}$	56	18 912	3% $^2H1$, 48% $^2H2$,	33	267
$\pi\sigma$	19 164		78	18 938	27% ^4G, 20% ^4I,		
$\pi\sigma$	19 214		78	18 972	2% ^4S		
σ	19 296		56	19 008			
$\pi\sigma$	19 312		78	19 004			
σ	19 327		56	19 025			
$\pi\sigma$	20 568	$\frac{7}{2}$	78	20 657	90% ^4F, 6% $^2G1$,	4	−94
			56	20 663	4% $^2G2$		
σ	20 660		56	20 754			
$\pi\sigma$	20 667		78	20 768			
σ	22 255	$\frac{5}{2}$	56	22 310	80% ^4F, 17% $^2D1$,	6	−51
σ	22 276		56	22 318	2% $^2D2$, 1% ^4S		
$\pi\sigma$	22 301		78	22 356			

TABLE V. *(Continued)*

Polarization	Expt.	J	Γ	Calc.	Wave functions	S	Δcg
$\pi\sigma$	22 625	$\frac{3}{2}$	56	22 553	58% ^4F, 22% $^2D1$,	5	77
$\pi\sigma$	22 656		78	22 578	20% ^4S		
$\pi\sigma$	24 533	$\frac{9}{2}$	78	24 019	17% $^2G1$, 14% $^2G2$,	15	508
			56	24 142	29% ^4F, 7% $^2H1$,		
$\pi\sigma$	24 650		78	24 163	15% $^2H2$, 15% ^4I,		
σ	24 706		56	24 188	3% ^4G		
$\pi\sigma$	24 757		78	24 273			

parameter. However, the final calculation was done with the free-ion value. ζ was given the value of 2445 cm^{-1} in this calculation, since this value gave the best (but not at all good) splitting between the multiplets of the ground term. The calculated energy of those levels determined experimentally are listed in Table V.

The calculated term composition of the wave functions of each multiplet are also given in Table V. The composition did not differ much from level to level within a multiplet. For many of the multiplets, the wave functions were so mixed that there is little value in assigning a single set of LS quantum numbers to them. Contrary to this LS mixing, the J mixing seems small. Hence, only the J values are given in Table V.

D. Discussion

The experimental energy levels of the ground term of Er^{3+} in $LiYF_4$ as reported by Brown *et al.*[11] are within a few cm^{-1} in agreement with those found in $LiErF_4$. Thus the crystal field cannot differ much from $LiYF_4$ to $LiErF_4$. Karayianis[2] fits the crystal-field parameters to the experimental result and achieves an rms deviation of 13.7 cm^{-1}, but there is an error in his assignment of levels for the $^4I_{9/2}$ multiplet. In term calculations the two levels just above 12 500 cm^{-1} come out in wrong order (compare Fig. 2). In the configuration calculation the order is correct.

In a later paper Karayianis *et al.*[3] give for Er^{3+} in $LiYF_4$ a new set of parameters from an unpublished work. These parameters deviate from the first set. The agreement with the parameters of the dense crystal is for both set of parameters poor. Calculated energy levels for multiplets outside the ground configuration have not been published for Er^{3+} in $LiYF_4$. The present configuration calculation for Er^{3+} in $LiErF_4$ gave good results for most of the multiplets below 26 000 cm^{-1}.

The mismatch between centers of gravity for the multiplets is as seen from Table V for most of the multiplets less than 100 cm^{-1} (or ~0.5%). Two multiplets for which the disagreement is considerably greater are $^4I_{13/2}$ and $^4I_{9/2}$ of the ground term. It is surprising that the agreement is so bad for the ground term, and that the agreement was better in the term calculation. $^4I_{13/2}$ could probably be brought to the right position by using a smaller value for ζ, but this would make the situation for $^4I_{9/2}$ worse. Calculations with some of the terms of the ground configuration omitted showed that the low value for $^4I_{9/2}$ is due to the mixing from the two ^2G terms. To moderate the effect of ^2G, configuration mixing must be taken into account.

The calculated multiplet splittings are for most of the multiplets in good agreement with the experimental splittings. As seen from Table V, the standard deviation for each multiplet, except for the two dominated by ^2H and ^2G, is comparable to the standard deviation obtained by fitting to the lowest levels. The common standard deviation for the three lowest terms ^4I, ^4F, and ^4S (with the center of gravity for the multiplets matched) is 5 cm^{-1}. Thus, even if the second set of B parameters for Er^{3+} was obtained by fitting to few levels only, these parameters gave good splittings of most of the multiple below 26 000 cm^{-1}.

For multiplets with large differences in crystal-field splittings, the mismatch between centers of gravity was also large, whereas the opposite was not always the case, i.e., if the wave functions of the multiplets are calculated correct, the crystal-field splittings will be correct too.

VI. CONCLUSION

The energy levels of Ho^{3+} and Er^{3+} in $LiRF_4$ found experimentally were in agreement with what could be expected from results on the ions diluted in $LiYF_4$, although some additional lines and broad absorption bands were seen in the case of $LiHoF_4$. Maybe the $LiHoF_4$ crystals have not been completely pure and perfect. The x-ray pictures showed perfect single crystals, but microscopic examination of the clear crystals revealed some opaque grains.

The relatively strong variation of level positions

TABLE VI. Crystal-field parameters in cm^{-1} for Er^{3+} in $LiErF_4$. (I) Found by fitting to the whole ground term. The uncertainty on these parameters is more than 50 cm^{-1}. (II) Found by fitting to only the two lowest multiplets. The uncertainty on these parameters is less than 10 cm^{-1}.

	B_{20}	B_{40}	B_{44}	B_{60}	B_{64}
I	312	−566	718	−56	514
II	377	−642	861	−71	625

with temperature, which was found for Tb^{3+} in $LiTbF_4$, has not been found for Ho^{3+} or Er^{3+} in $LiRF_4$. Temperature-dependent crystal-field parameters are thus not a common feature of $LiRF_4$ crystals or in any case the effect is not nearly as strong for some of the crystals as for $LiTbF_4$. The reason for this is not evident.

The calculations showed that the term mixing is considerable. In fact, for many of the multiplets no single term is predominant. This mixing affects strongly the positions of the multiplets and to a lower degree also the crystal-field splittings of these. The mixing of the ground term with other terms influenced the spin-orbit splitting of the ground term so much that it was not possible to give this splitting correctly in a ground-term calculation with the effective spin-orbit Hamiltonian given in Eq. (2) extended to third order. This is in contrast to the situation for Tb^{3+}, where the ground term is well isolated from other terms.

For Ho^{3+} it was possible to fit the crystal-field parameters to give good splittings for all the multiplets of the ground term in the term calculation. In the case of Er^{3+} the mixing of the ground term with other terms was so strong that it was not possible to get good crystal-field splittings of the multiplets in the ground-term calculation. It was, however, in the configuration calculation of Er^{3+} possible to get good splittings of most of the lowest multiplets with crystal-field parameters found by fitting to only some of the multiplets of the ground term.

Even in the configuration calculation it was not possible to give the multiplets the right positions. The approximation to let the matrix elements of the electrostatic interaction depend on only one parameter (F_2) instead of three cannot give errors which are comparable to the mismatch found here. Hence, in order to get better results it will be necessary to account for configuration mixing.

The crystal-field parameters obtained for Ho^{3+} and Er^{3+}, respectively, were within the range of earlier reported parameters. They were closer to the parameters found by spectroscopic investigation of the ions diluted in $LiYF_4$ (Refs. 2 and 3) than to the parameters found from the magnetic susceptibility of the dense crystals.[5] A more detailed comparison will be given in a later paper, when more spectroscopically determined crystal-field parameters for the dense crystals are available.

It is, however, by now clear that the spectra obtained for the dense crystals do not differ much from the spectra of the ions diluted in $LiYF_4$. The crystal-field splittings of the multiplets are in qualitative agreement and the linewidths observed in the dense crystals are for most of the lines still small compared to the splitting. This means that one may substitute heavy rare-earth ions for Y ions in $LiYF_4$ without deforming the lattice drastically and that the R^{3+}-R^{3+} interaction in $LiRF_4$ is weak. This indicates that $LiY_{1-x}R_xF_4$ crystals may be of value as fluorescence systems with high concentration of the active ion.

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